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Atomic force microscopy on polymers and polymer related compounds

1. Cold-extruded polyethylene

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ABSTRACT

Results of Atomic Force Microscopy (AFM) studies on cold-extruded polyethylene (PE) are presented. AFM images from the range 700 x 700 nm down to the atomic scale were obtained on a flat surface, which was prepared by cutting a rod-like sample along the extrusion direction. Large scale AFM micrographs of PE reveal the fibrillar morphology of the uniaxially oriented material. Microfibrils with diameters in the range 20-90 nm are aligned parallel to the extrusion direction. In the smaller scale images the oriented patterns were assigned to the individual polymer chains. The surface texture pattern shows chain overlapping as a result of the extrusion process. Parts of extended chains were also found. AFM responses of individual methylene groups have been resolved.

INTRODUCTION

Up until now it has been possible to obtain images of the molecular structure of polymer materials by scanning tunneling microscopy, STM, and atomic force microscopy, AFM, only in a limited number of cases. Electrical conductivity of the investigated sample is a crucial requirement for STM [1], and STM studies with an atomic resolution have been restricted to a number of conductive polymers [2-4] and polymer based materials such as carbon fibers [5]. Non-conductive surfaces of polymeric materials can be imaged by STM after coating them with a thin metallic or carbon layer. This technique was used to study the surface of PE samples [6]. However, the structure resolution is restricted in this case due to the coating, and STM cannot be exploited for the imaging of small scale surface structures in the Ångstrom range. Therefore, results obtained in this way may be regarded as complementary to scanning electron microscopy studies.

In another approach non-conductive materials were studied by STM when a thin organic layer was deposited on a conductive substrate (graphite monocrystal or a noble metal surface). It was possible to obtain STM images from up to 100 nm thick n-alkane layers on graphite [7]. The patterns found were assigned to microcrystal domains. An exceptional and unique atomic resolution was achieved in images of liquid crystalline films on graphite [8].

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Although the nature of STM imaging of non-conductive layers is still a puzzle, application of this approach can be valid for polymers. However, in such cases, it remains a crucial question, to which extent the conformation of the observed polymer is influenced by interaction with the substrate. Certainly, only direct comparison of surface structure with the bulk would allow unequivocal conclusions.

AFM is based on the registration of the interatomic forces which act between the top atoms of a sharp microscopic pyramid, the actual probe, and the surface atoms. Electrical conductivity of the sample is not especially required. Thus AFM is intrinsically more suitable for the investigation of polymer materials than STM. First AFM studies of surfaces of inorganic and organic materials [9-11] demonstrated that images with atomic resolution can be obtained and that examination of polymers and their low molecular weight homologues is a promising task. Dendritic crystals of PE [12] have also been studied by AFM. Molecular resolution of the surface structure, however, has not been described. Recently, the molecular scale ordering has been registered in AFM images of monocrystal surfaces of organic charge transfer complexes and normal and cyclic alkanes [13-14].

In the present communication, AFM studies on a cold extruded PE rod are reported. In this case, surfaces parallel to the extrusion direction are formed by essentially extended zig-zag chains. The expected ordering of polymer chains is favourable for AFM detection and interpretation of images.

EXPERIMENTAL

AFM experiments at ambient conditions were carried out with a Nanoscope II microscope (Digital Instruments, Inc., Santa Barbara, CA, USA). The sample is fixed on the cylindrical piezodrive and scanned beneath a tiny pyramidal Si_3N_4 tip. This tip is attached to a microfabricated cantilever (200 μm triangular base). During scan, deflections of the cantilever are proportional to variations of the interaction force between tip and surface. They are registered via reflection of a laser beam, which is pre-aligned onto the backside of a cantilever. The piezo drive is guided by an electronic feedback mechanism which allows the surface to be scanned with constant force. The resulting profile yields the three dimensional AFM image which is represented by an array of 400 x 400 points and color or grey scale coded z-variations (z indicates the direction perpendicular to the examined surface). Elevated spots in an atomic force image correspond to maximum repulsive force and, consequently, to surface atoms or atom groups. The applied AFM probe (type A) had a largest scan area of 700 x 700 nm. Cantilevers with a force constant of .06 and .12 N/m were used. Scanning line frequencies were 1Hz for large scale scans and up to 39 Hz for scanning smaller areas. The z-changes are normalized in height or force units depending on the imaging mode. Only low pass filtering was applied in order to improve AFM images, unless especially stated.

An important requirement for samples to be studied by AFM is flatness of the surface. The grown and cleaved surfaces of monocrystals appeared to be appropriate for examination. Different methods of surface preparation of polymer samples - spin-casting, Langmuir-Blodgett techique, ultramicrotomy and others - should also be tested from the methodological viewpoint. AFM samples from the rod-like, cold extruded PE were prepared by ultra-microtomy. Pieces of the extruded PE were embedded in an epoxy resin (Epon 812, Serva) and cut parallel to the extrusion direction by means of a Reichert-Jung Ultracut E microtome at room temperature. In this way a flat, glossy surface could be obtained. PE samples were fixed to the AFM stainless steel support by cyanoacrylate glue.

RESULTS AND DISCUSSION

All large scale AFM images (700 x 700 nm), which were obtained from different areas of the PE surface, show similar features. Elongated elevations are aligned along the extrusion direction (Fig. 1). The changes of the angle of rotation of the scan relative to the sample - this possibility is an important feature of the applied instrument - have led to the consequent variations in the direction of the AFM patterns. They can be assigned to the microfibrils of PE. Their cross-section ranges from 20 to 90 nm and varies from place to place (Fig. 1, upper part). Most of the microfibrils are longer than the scan size (700 nm). However, AFM scans up to 100 μm are possible, and these measurements are in progress. It is difficult to judge how well the real surface profile is reproduced in the AFM images. The sharpness of the 45° tip does not permit the steep and rather deep grooves to be followed exactly.

AFM images of smaller scans reveal the structural details of microfibrils. In the 13 x 13 nm image (Fig. 2) one can distinguish patterns aligned along the main fibril direction. The width of these rows of 'hills' are in the range from 0.4 to 0.5 nm. This is in fair agreement with the estimated diameter of extended PE chains in the trans conformation, when the van der Waals radii of the hydrogen atoms are taken into consideration. Thus, we can assign the rows of AFM patterns to the individual polymer chains. The preferential orientation of the PE chain axis parallel to the extrusion direction has been revealed by different physical methods and is visualized now by AFM. The Fourier Transform (FT) picture of the image Fig. 2 (below this figure) clarifies the chain ordering. Fig. 3 presents the corresponding 3D-picture. The sub-Å z-resolution appears remarkable. A frequency filtration in Fourier space - only the main frequency patterns have been saved - and subsequent restoration of an image yield the picture shown in Fig. 4. The obtained texture pattern shows how polymer chains are mingled and oriented during solid-state extrusion. Such information may be extremely important for consideration of the molecular mechanism of polymer orientation.

In several places of the polymer surface parts of extended chains were registered. Fig. 5 demonstrates several chains, the central one being in all-trans conformation. This conclusion is supported by the correspondence of repeat distances along the chain (see left of Fig. 4D) with the separation between CH_2 groups of 2.5 Å, in the all-trans conformation of PE. This means that the conformational order of the polymer can be examined by AFM.

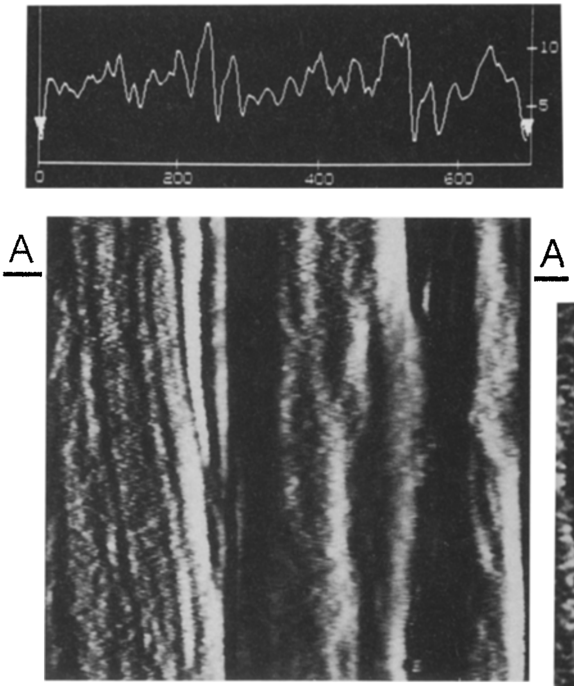

Figure 1: Large scale top-view image of cold-extruded PE - area 660 x 660 nm. White spots correspond to elevations in the z-direction. The contour along A-A direction is shown in upper part

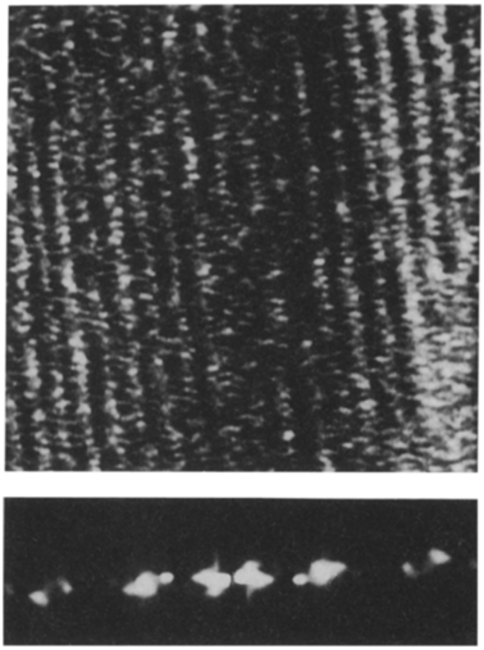

Figure 2: AFM top-view image of an 8.8 x 8.8 nm area on the surface of cold-extruded PE, and - below - fast two-dimensional Fourier transform picture

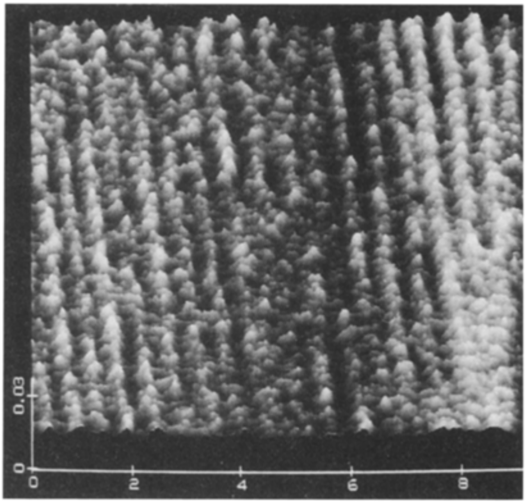

Figure 3: Three-dimensional surface presentation of cold-extruded PE, viewed from an angle of 60°, width and height in nm

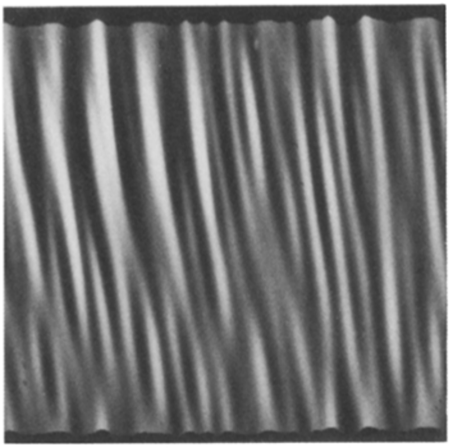

Figure 4: Restoration of a two-dimensional surface view, after filtration in Fourier space, width 12.5 nm

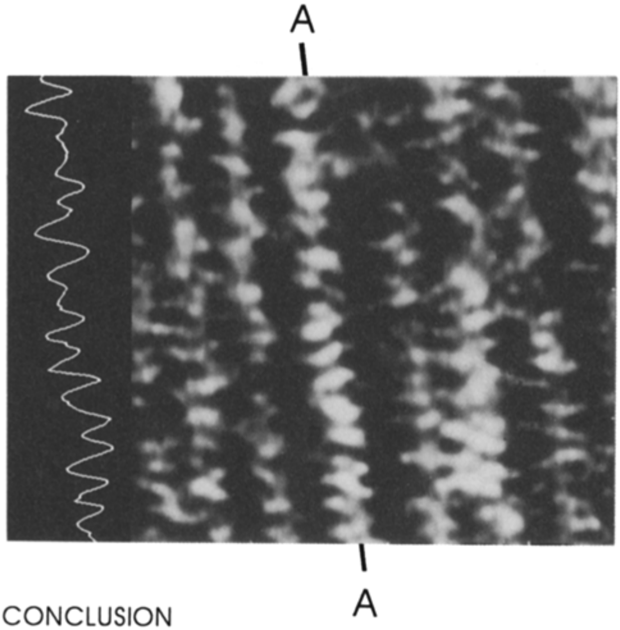

Figure 5: Atomic scale AFM image of part of PE surface - width 3.6 nm - Contour along A-A direction presented at left

CONCLUSION

The results presented above demonstrate the capability of atomic force microscopy experiments for surface structure analysis of polymers on the atomic scale. Thus, typical features of the polymer structure, i.e. stems, have been observed. The atomic scale images of polyethylene give grounds for direct visualization of conformational order and different defects in chain molecules. Generally, AFM offers novel and unique perspectives for surface studies on polymers. In addition to the characterization of the supermolecular structure beyond the limits of conventional electron microscopy, the molecular organization can be directly depicted on the atomic scale. In combination with temperature variations it should be possible to obtain new insight into the motional state of macromolecules at the surface of bulk materials.

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